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(54) **Leak detection and responsive treatment in industrial water processes.**

(57) Leakage is detected between a process fluid and a temperature-conditioning fluid, or from a process fluid to a temperature-conditioning fluid, in an industrial process. The industrial process includes an A and a B fluid, and one of the A and B fluids receives heat from or transfer heat to the other of the A and the B fluids by an indirect contact method, and one but not both of the A and the B fluids is an industrial process fluid. At least one specie of tracer chemical is maintained in the A fluid, and that specie of tracer chemical is not a normal component of the B fluid. At least one of the A and the B fluids is subjected to at least one analysis at least one site. Such analysis at least detects the presence of the specie of tracer chemical when the fluid subjected to the analysis is the B fluid, and such analysis at least determines the concentration of the specie of tracer chemical when the fluid subjected to the analysis is the A fluid.

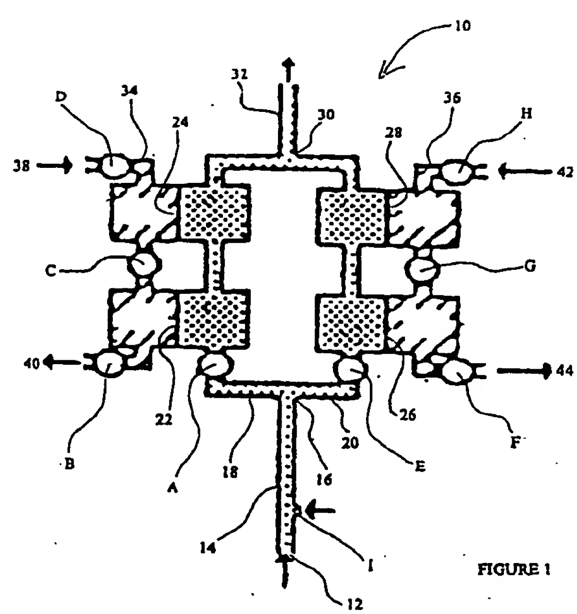

FIGURE 1

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teurization waters, and the like. The primary function of temperature-conditioning fluids is that of a heat source or heat receiver, and therefore there seldom would be any practical reason for employing a fluid other than water, but the use of some other fluid as the temperature-conditioning fluid does not exclude the applicability of the process of the present invention for that reason alone. The process of the present invention in broad embodiment is not dependent on the specific type of temperature-conditioning fluid.

Temperature-conditioning fluids and process fluids are generally brought into indirect contact for the purpose of heat transfer from the source fluid (which is the process fluid in a cooling water system) to the receiver (which is the cooling water in a cooling water system), during which heat transfer process the fluids are separated by a barrier that is a good conductor of heat, which barrier is called the heat transfer surface. An assembly comprised of at least one heat transfer barrier, which barrier has a process fluid side and a cooling fluid side, in a containment vessel, is called a heat-exchanger. A simple heat-exchanger may be comprised of a tube or pipe located concentrically inside of another (the shell). In such a shell-and-tube heat-exchanger the process fluid typically flows through the inner pipe, and the cooling fluid flows through the annulus between the inner pipe and the shell. In a parallel or cocurrent flow heat-exchanger, both fluid streams flow in the same direction. In a countercurrent flow heat-exchanger, the fluid streams flow in opposite directions. Regardless of the type or complexity of a heat-exchanger, a characteristic common to all is transfer of heat across a heat transfer surface that has a process fluid side and an opposite cooling fluid side.

In a food processing process, the process fluid may be contained in one or a plurality of enclosed containers, such as jars or bottles, which are immersed in an elevated temperature-conditioning fluid, such as cooking or pasteurization waters, and the heat is transferred from the temperature-conditioning fluid across the wall(s) of the containers. Such an assembly can, and herein is, also considered a heat-exchanger.

Leakage between a temperature-conditioning fluid and a process fluid most commonly occurs within a heat-exchanger because within a heat-exchanger there is generally only a single heat exchange surface or wall separating the fluid bodies. Moreover, there generally is a temperature gradient across such surface or wall and a significant stream flow along at least one side of such surface or wall, which conditions create material stresses that can lead to ruptures. Leakage between a temperature-conditioning fluid and a process fluid can of course also occur elsewhere, such as when such fluids are held or flow through vessels or lines or the like that have contiguous walls, or when a normally-closed flow path between such vessels or lines or the like is in some way breached. The process of the present invention in broad embodiment is not dependent on the specific type of leakage site, and instead is applicable to any water industry process having a process fluid and a temperature-conditioning fluid that are normally, or desirably, kept isolated from each other to avoid any cross-contamination.. although such fluids would commonly be brought into close proximity (indirect contact) for heat exchange purposes.

Regardless of how leakage occurs, the dissimilarity between such fluids generally is a controlling factor as to the gravity of the problem(s) created by cross-contamination. For instance, pasteurization water is normally free of organic nutrients, and thus is not normally treated with biocide to control microbial growth. If a product container ruptures during the pasteurization process however, the product fluid released into such waters could well contain sufficient nutrient to trigger microbial growth and seriously foul such water. In many industries employing cooling water systems, the process streams contain significant amounts of hydrocarbons which would lead to cooling water fouling if leaked to the cooling water stream or basin. In many industries employing cooling water systems, cooling waters are treated with corrosion inhibitors, scale inhibitors, possibly biocides, and other agents, and while such agents are generally present in cooling waters in only minute amounts, even extremely minute amounts thereof may be sufficient to seriously taint the material in the process waters. Cross-contamination between temperature-conditioning fluids and process fluid can lead to such grave problems that the choice of temperature-conditioning fluid treatment agents may be limited to those agents having less potential for harm but less than optimum treatment effectiveness. The process of the present invention may in some instances open such limitations to more effective agents.

As noted above, a very simple heat-exchanger may be comprised of concentric tubing, and in most industrial plants a heat-exchange system is comprised of more complex heat-exchangers and/or a plurality of heat-exchangers. The walls of the multitude of lines and/or vessels cannot conveniently be examined on a routine basis for ruptures or other breaches. Such an examination would require disruption of the process and often an extensive disassembly of the system. Leakage detection between te perature-conditioning fluids and process fluid termining the site(s) of leakage, and/or qu the degree of leakage through the pro present invention will minimize contamination potential and mini disruption and/or system disas leviate the cross-contamina

In addition, in an em vention the process

substances or categories of substances at low concentrations is desired or required, such as often is the case for the process of the present invention, the filters are set for a specific combination of excitation and emission wavelengths, selected for substantially optimum low-level measurements.

Fluorescence emission spectroscopy is one of the preferred analysis techniques for the process of the present invention. Certain compounds that normally occur in either the temperature-conditioning fluid or the process fluid are inherently tracers for a fluorescence analysis. For example, aromatic hydrocarbons are components of some process fluids, including hydrocarbon-containing process streams and process fluids held in discrete containers. Foodstuffs may contain one or more components that readily fluoresce, such as beer which has been found to test positive for fluorescence analysis and thus leakage by bottle breakage during pasteurization can be readily detected and quantified by fluorescence monitoring of the pasteurization waters, and activate a responsive feed of biological control agents or the like to such waters to lessen the harmful effects of contamination by a nutrient-containing substance. Some naturally fluorescent compounds are also water treatment agents, and thus may be among the normal components of cooling waters, such as aromatic organic corrosion inhibitors, such as aromatic(thio)(tri-)azoles. Some water treatment agents may be susceptible to tagging with fluorescent groups, for instance as disclosed in U.S. Patent No. 5,128,419, D. W. Fong and J. E. Hoots, issued July 7, 1992, incorporated herein by reference, wherein the tagging of polymers with pendant fluorescent groups by (trans)amidation derivatization of pre-existing polymers having carbonyl-type pendant groups is disclosed. Water-treatment polymers tagged with pendant fluorescent groups may of course be prepared by methods other than (trans)amidation derivatization. Other fluorescent chemical tracers and monitoring techniques are now known, for instance as disclosed in U.S. Patent No. 4,783,314, J. E. Hoots and B. E. Hunt, issued November 8, 1988, incorporated herein by reference, wherein inert fluorescent tracers are employed in combination with a fluorescence monitoring, such as the sodium salt of 2-naphthalenesulfonic acid and Acid Yellow dye.

In general for most fluorescence emission spectroscopy methods having a reasonable degree of practicality, it is preferable to perform the analysis without isolating in any manner the fluorescent tracer. Thus there may be some degree of background fluorescence. In instances where the background fluorescence is low, the relative intensities (measured against a standard fluorescent compound at a standard concentration and assigned a relative intensity for instance 100) of the fluorescence of the tracer versus the background can be very high, for instance a ratio of 100/10 or 500/10 when certain combinations of excitation and emission wavelengths are employed even at low fluorescent compound concentrations, and such ratios would be representative of relative performance (under like conditions) of respectively 10 and 50. For most cooling water backgrounds, a compound that has a relative performance of at least about 5 at a reasonable concentration is very suitable as a fluorescent tracer itself or as a tagging agent for water treatment polymers and the like when such compounds contain an appropriate reactive group for the tagging reaction. When there is or may be a specific chemical specie of reasonably high fluorescence in the background, the tracer and the excitation and/or emission wavelengths often can be selected to nullify or at least minimize any interference of the tracer measurement(s) caused by the presence of such specie.

One method for the continuous on-stream monitoring of chemical tracers by fluorescence emission spectroscopy and other analysis methods is described in U.S. Patent No. 4,992,380, B. E. Moriarity, J. J. Hickey, W. H. Hoy, J. E. Hoots and D. A. Johnson, issued February 12, 1991, incorporated hereinto by reference.

Combined HPLC-Fluorescence Analysis

The combination of high-pressure liquid chromatography ("HPLC") and fluorescence analyses of fluorescent tracers is a powerful tool for the present leak detection process, particularly when very low levels of the fluorescent tracer are used or the background fluorescence encountered would otherwise interfere with the efficacy of the fluorescence analysis. The HPLC-fluorescence analysis method allows the tracer compound to be separated from the fluid matrix and then the tracer concentration can be measure. The combination of HPLC-fluorescence analysis is particularly effective for measuring minute levels of tracer in highly contaminated fluids.

The HPLC method can also be effectively employed to separate a tracer compound from a fluid matrix for the purposes of then employing a tracer-detection method other the fluorescence analysis, and such other tracer-detection methods include without limitation light absorbance, post-column derivatization, conductivity and the like.

Colorimetry Analysis

Colorimetry or spectrophotometry may be employed to detect and/or quantify a chemical tracer. Colorimetry is a determination of a chemical specie from its ability to absorb ultraviolet or visible light. One colorimetric analysis technique is a visual comparison of a blank or standard solution (containing a known concentration of the tracer specie) with that of a sam-

bodiment, the chemical compound(s) selected as the tracer should be soluble in at least one, and more preferably in both, of the temperature-conditioning fluid and process fluid of the industrial process, at least at the concentration level(s) expected in the respective fluid. For instance, a tracer may be fed to a temperature-conditioning fluid and its presence monitored in the process fluid, where its appearance would result only from leakage. The expected concentration in the process fluid upon such leakage occurring would of course be much less than the concentration of such tracer fed to, or maintained, in the temperature-conditioning fluid. If however only the decrease of tracer concentration in the fluid to which it is fed is to be monitored, its solubility in the other fluid is generally irrelevant. In preferred embodiment, the chemical compound(s) selected as a tracer should be either stable in the environment of at least one of the fluids, and preferably both of the fluids, for the useful life expected of the tracer, or its loss from the fluid due to degradation, deposition, complexation, or other phenomena should be predictable and compensative, particularly when it is desired not merely to detect the presence of some amount of the tracer, but also to determine the concentration thereof, or change in concentration. In preferred embodiment, the combination of the chemical compound(s) selected as the tracer and the analytical technique selected for determining the presence and/or concentration of such tracer, should permit such determination(s) without isolation of the tracer, and more preferably should permit such determination(s) on a continuous and/or on-line basis. In preferred embodiment, the analytical technique(s) selected for determining the presence and/or concentration of a tracer, should permit such determination(s) to provide a signal that can activate or regulate the feed of an appropriate treatment chemical(s) to the fluid being contaminated by virtue of the leak detected by the technique.

One embodiment the process of the present invention is comprised of adding a chemical tracer to one, but preferably not both, of the temperature-conditioning fluid and the process fluid, and monitoring the concentration of such tracer in the fluid to which it was added by an analytical technique effective for such tracer, and in preferred embodiment when the same fluid both receives the tracer feed and is subjected to the monitoring, the monitoring is conducted to determine any decrease in the concentration of the tracer in the receiving fluid across at least one potential leakage site, such as a heat-exchanger. In another and preferred embodiment the process of the present invention is comprised of adding a chemical tracer to one, but preferably not both, of the temperature-conditioning fluid and the process fluid, and monitoring the concentration of such tracer in the other fluid by an analytical technique effective for such tracer, and in preferred embodiment when the one fluid receives the tracer feed while the other is subjected to the monitoring, the monitoring is conducted to determine at least any appearance, and more preferably the concentration, of the tracer in the monitored fluid across at least one potential leakage site, such as a heat-exchanger. In further preferred embodiments, when the industrial process system has more than one potential leakage site, such as a heat-exchanger, the aforesaid monitorings are conducted across more than one of such potential leakage sites, and more preferably substantially across each of such potential leakage sites or heat-exchangers. By monitoring across separate heat-exchangers in bank of heat-exchangers, the location(s) of the leakage among such heat-exchangers can be determined, and the extent of leakage (rate of leakage), at separate leakage sites, may also be determined.

Example 1

Cooling water had been leaking into a monoethanolamine/water process stream ("MEA stream") of an industrial plant for several years. Such leakage necessitated frequent cleanups of the process stream, which significantly increased the operating costs of the plant. The site of the leakage was believed to be through one or more of the heat-exchangers in a bank of four heat exchangers and/or a separate beat-exchanger. The total cooling water leakage rate was known to be on the order of tenths of gallons per minute, which represents an extremely small volume of water per unit time in comparison to the flow rates of the process and cooling water streams (which were respectively about 1,000 and about 10,000 gallons per minute). The difficulty of site location of such a relatively small leakage was heightened by the possibility that the leakage was divided among a plurality of heat-exchangers. Complicating the use of a fluorescent compound to trace the location(s) of such leakage was the composition of the process stream, which contained treatment chemicals and other dissolved substances that fluoresced and exhibited high absorbance of ultraviolet light. The layout of the bank of four heat-exchangers is shown diagrammatically in FIGURE 1, in which the bank of heat-exchangers is designated generally by the reference numeral 10. The collateral industrial stream is the cooling water stream that flows through the cooling water lines from a cooling water inlet 12 through a first main line 14 to a first junction 16 whereat the first main line 14 divides into a west leg line 18 and an east leg line 20. The cooling water stream flowing through the west leg line 18 serves the southwest heat-exchanger 22 and then the northwest heat-exchanger 24. The cooling water stream flowing through the east leg line 20 serves the southeast heat-exchanger 26 and then the northeast heat-exchanger 28. The west leg line 18 and the east

Generally it is desirable to employ the least amount of tracer chemical that is practical for the circumstance, and the amount of the tracer added to the fluid should be at least an amount effective for the determinations desired. Seldom would a tracer be deliberately fed to a fluid in an amount grossly in excess of the minimum effective amount because there generally would be no practical purpose in doing so that would justify the costs involved and any deleterious effects on the quality of either of the fluids caused by the presence of the tracer chemical therein. The amount of tracer chemical to be added to the tracer-receiving fluid that is effective without being grossly excessive will vary with a wide variety of factors, including without limitation the tracer and monitoring method selected, the potential for background interference with the selected monitoring method, the magnitude of the suspected or potential leakage, the monitoring mode (on-line continuous, semi-continuous, slug-and-sample, and the like). Generally the dosage of tracer to one or the other of the fluids will be at least sufficient to provide a concentration of tracer therein of about 0.1 ppm, and more commonly at least about 10 or 100 ppm or higher.

In one embodiment, the present invention is a process for detecting leakage from a process fluid to a temperature-conditioning fluid in an industrial process wherein the industrial process includes a process fluid and a temperature-conditioning fluid and the temperature-conditioning fluid receives heat from or transfers heat to the process fluid by an indirect contact method, comprising;

maintaining in the process fluid at least one specie of tracer chemical, which specie of tracer chemical is not a normal component of the temperature-conditioning fluid;

subjecting at least one of the process fluid and the temperature fluid to at least one analysis at least one site; and

wherein the analysis at least detects the presence of the specie of tracer chemical when the fluid subjected to the analysis is the temperature-conditioning fluid, and wherein the analysis at least determines the concentration of the specie of tracer chemical when the fluid subjected to the analysis is the process fluid.

The present invention in another embodiment is a process for detecting leakage between a process fluid and a temperature-conditioning fluid in an industrial process wherein the industrial process includes an A and a B fluid, and one of the A and B fluids receives heat from or transfers heat to the other of the A and the B fluids by an indirect contact method, and one but not both of the A and the B fluids is an industrial process fluid, comprising;

maintaining in the A fluid at least one specie of tracer chemical, which specie of tracer chemical is not a normal component of the B fluid;

subjecting at least one of the A and the B fluids to at least one analysis at least one site; and

wherein the analysis at least detects the presence of the specie of tracer chemical when the fluid subjected to the analysis is the B fluid, wherein the analysis at least determines the concentration of the specie of tracer chemical when the fluid subjected to the analysis is the A fluid, and

wherein at least a detection of the specie of chemical tracer activates or modifies a signal, and the signal upon activation or modification activates or modifies a feed of at least one treatment chemical to the B fluid, wherein the treatment chemical feed upon activation or modification is effective to at least lessen at least one deleterious effect of a leakage of a portion of the A fluid into the B fluid.

The present invention in another embodiment is a process for detecting a leakage site between a process fluid and a temperature-conditioning fluid in an industrial process wherein the industrial process includes an A fluid and a B fluid normally held respectively within an A means of containment and a B means of containment, and one of the A and B fluids normally receives heat from or transfers heat to the other of the A and the B fluids by an indirect contact method, and one but not both of the A and the B fluids is an industrial process fluid, comprising;

maintaining in at least one segment of the A containment means at least one specie of tracer chemical; and

determining the site at which the specie of tracer chemical appears within the B containment means,

particularly wherein the appearance of the specie of chemical tracer is determined by fluorescence analysis and/or wherein the segment of the A containment means is a heat-exchanger.

In certain preferred embodiments, the specie of chemical tracer is a normal component of the A fluid or process fluid. In certain preferred embodiments, the specie of chemical tracer is a synthetically tagged normal component of the A fluid or process fluid, for instance such as when a polymeric water treatment agent is tagged with pendant fluorescent groups by post-polymerization derivatization, as discussed above. In certain preferred embodiments, the specie of chemical tracer is foreign to the normal components of the A fluid or process fluid, for instance when an inert tracer is added for the purposes of present invention, or both for the purposes of the present invention and for the purposes of a distinct tracer process. In certain preferred embodiments, the specie of chemical tracer is at least one fluorescent compound and the analysis at least includes fluorescence analysis, which is particularly preferred because of the ease at which such method can be used for on-line continuous or semi-continuous monitoring, and other known advantages.

chemical tracer is a normal component of said process fluid or a synthetically tagged normal component of said process fluid or is foreign to the normal components of said process fluid.

3. The process of Claim 1 or Claim 2 wherein said analysis determines a spectral or chemical characteristic of said specie of chemical tracer that is proportional to the concentration of said specie of chemical tracer in the fluid analyzed.

4. The process of Claim 1, Claim 2 or Claim 3 wherein at least one of said process fluid and said temperature-conditioning fluid is subjected to a plurality of said analyses across a suspected or potential site of leakage.

5. The process of Claim 4 wherein said process fluid and said temperature-conditioning fluid are fluid streams that each flow through a side of each of a plurality of heat-exchangers, and wherein at least one of said process and said temperature-conditioning fluids is subjected to a plurality of said analyses and at least two of said plurality of said analyses are conducted across at least one of said plurality of heat-exchangers.

6. The process of any one of the preceding claims wherein said specie of chemical tracer is at least one fluorescent compound and said analysis at least includes fluorescence and is an on-line continuous or semi-continuous analysis.

7. A process for detecting leakage between a process fluid and a temperature-conditioning fluid in an industrial process wherein said industrial process includes an A and a B fluid, and one of said A and B fluids receives heat from or transfers heat to the other of said A and said B fluids by an indirect contact method, and one but not both of said A and said B fluids is an industrial process fluid, comprising;

maintaining in said A fluid at least one specie of tracer chemical, which specie of tracer chemical is not a normal component of said B fluid;

subjecting at least one of said A and said B fluids to at least one analysis at least one site; and

wherein said analysis at least detects the presence of said specie of tracer chemical when said fluid subjected to said analysis is said B fluid, wherein said analysis at least determines the concentration of said specie of tracer chemical when said fluid subjected to said analysis is said A fluid, and

wherein at least a detection of said specie of chemical tracer activates or modifies a signal, and said signal upon activation or modification activates or modifies a feed of at least one treatment chemical to said B fluid, wherein said treatment chemical feed upon activation or modification is effective to at least lessen at least one deleterious effect of a leakage of a portion of said A fluid into said B fluid.

8. The process of Claim 7 wherein said specie of chemical tracer is a normal component of said A fluid or a synthetically tagged normal component of said A fluid or is foreign to the normal components of said A fluid.

9. The process of Claim 7 or Claim 8 wherein said specie of chemical tracer is at least one fluorescent compound and said analysis at least includes fluorescence analysis.

10. The process of Claim 7, Claim 8 or Claim 9 wherein said analysis is an on-line continuous or semi-continuous analysis of the B fluid.

11. The process of any one of Claims 7 to 10 wherein said A fluid and said B fluid are fluid streams that each flow through a side of each of a plurality of heat-exchangers, and wherein at least one of said A and said B fluids is subjected to a plurality of said analyses and at least two of said plurality of said analyses are conducted across at least one of said plurality of heat-exchangers.

12. The process of any one of Claims 7 to 11 wherein said analysis determines a spectral or chemical characteristic of said specie of chemical tracer that is proportional to the concentration of said specie of chemical tracer in the fluid analyzed.

13. The process of any one of Claims 7 to 12 wherein said treatment chemical is a biocide.

14. A process for detecting a leakage site between a process fluid and a temperature-conditioning fluid in an industrial process wherein said industrial process includes an A fluid and a B fluid normally held respectively within an A means of containment and a B means of containment, and one of said A and B fluids normally receives heat from or transfers heat to the other of said A and said B fluids by an indirect contact method, and one but not both of said A and said B fluids is an industrial process fluid, comprising:

maintaining in at least one segment of said A containment means at least one specie of tracer chemical; and

determining the site at which said specie of tracer chemical appears within the B containment means.

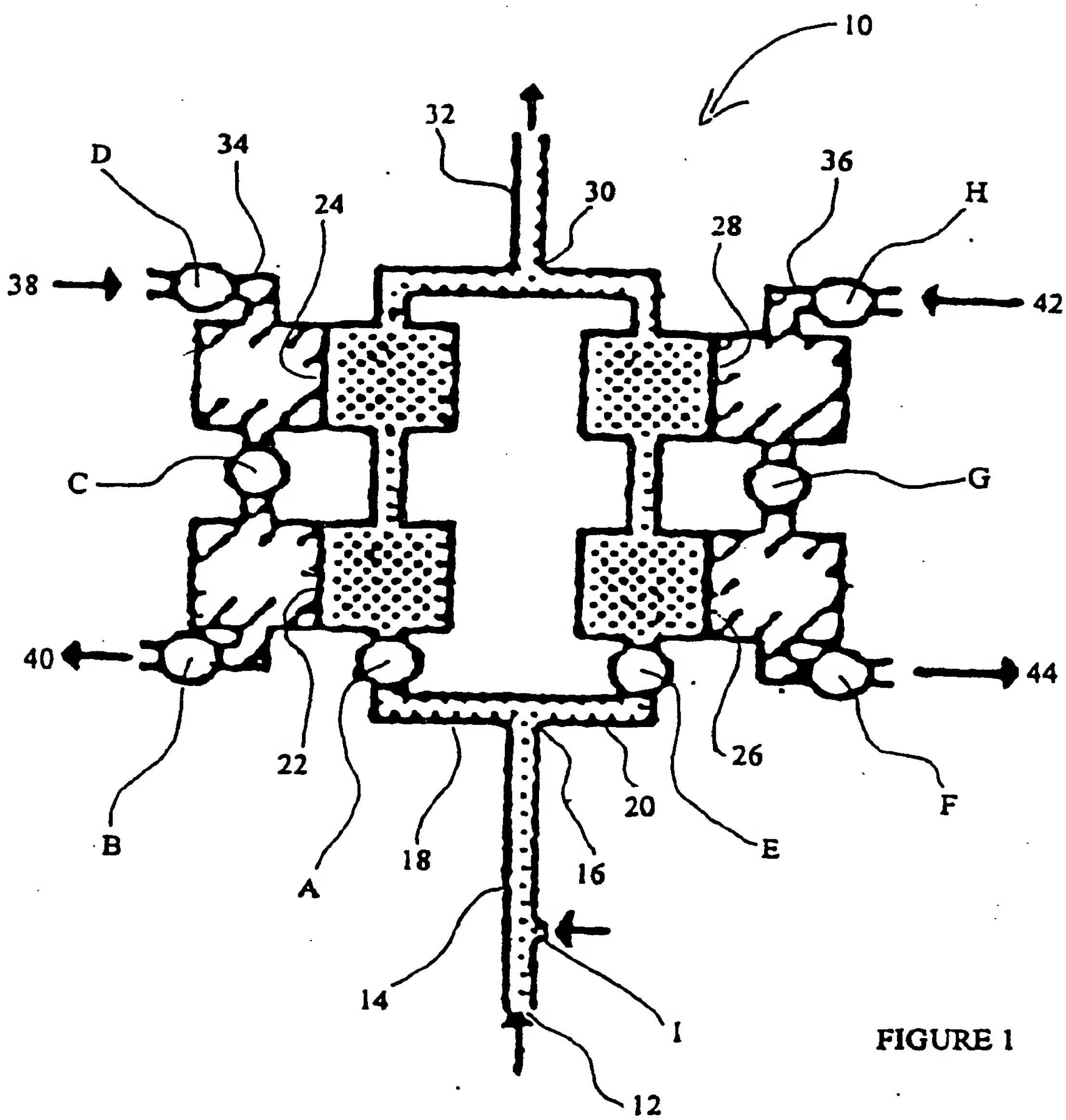

FIGURE 1